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SECONDARY BATTERY AND ITS ELECTRODE [Niji Denchi narabini Sono Denkyoku]

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SPECIFICATION

I. Title of the Invention
Secondary Battery and Its Electrode

II. Claims

 An electrochemical secondary battery which is characterized by using a polymer of amines expressed by a general formula (I)



[here, X and Y are selected independently from a set composed of chlorine, bromine, iodine, methyl and ethyl groups, ℓ and m are arbitrary integers selected independently within a range of 0 ~ 2, and then R is a hydrogen atom, an alkyl, an alkenyl and a $-C_6H_4-(Z)_n$ group (Z is selected from a set composed of chlorine, bromine, iodine, methyl and ethyl groups, and then n is an arbitrary integer within a range of 0 ~ 2) in at least one electrode.

¹ Numbers in the margin indicate pagination in the foreign text.

- 2. The secondary battery according to Claim 1 wherein the amines are amines with ℓ and m=0 and, in case of $R=-C_6H_4-(2)_{\rm B}$, n is also 0 in the general formula (I).
- 3. The secondary battery according to Claim 1 or 2 wherein the positive electrode is the polymer of amines.
- 4. An electrode for the electrochemical secondary battery which is characterized in that a polymer of amines expressed by a general formula (I)

[here, X and Y are selected independently from a set composed of chlorine, bromine, iodine, methyl and ethyl groups, ℓ and m are arbitrary integers selected independently within a range of 0 ~ 2, and then R is a hydrogen atom, an alkyl, an alkenyl or a - C_6H_4 -(Z)_n group (Z is selected from a set composed of chlorine, bromine, iodine, methyl and ethyl groups, and then n is an arbi-

trary integer within a range of 0 \sim 2) in at least one electrode is an electrode constructing material.

/2

5. The electrode according to Claim 4 wherein the amines are amines with ℓ and m=0 and, in case of $R=-C_6H_4-(Z)_n$, n is also 0.

III. Detailed Description of the Invention

[Field of Industrial Application]

The present invention relates to an electrochemical secondary battery with an organic polymer as an electrode material and an electrode used therein and, particularly, it is characteristic in that a thermoplastic polymer soluble in organic solvents is used as an electrode material. In more detail, the present invention relates to an electrochemical secondary battery which is characterized by using a polymer of amines expressed by a general formula (I)

(here, X and Y are selected independently from a set composed of chlorine, bromine, iodine, methyl and ethyl groups, ℓ and m are arbitrary integers selected independently within a range of 0 ~ 2, and then R is a hydrogen atom, an alkyl, an alkenyl and a $-C_0H_4-(Z)_n$ group (Z is selected from a set composed of chlorine, bromine, iodine, methyl and ethyl groups, and then n is an

arbitrary integer within a range of 0 \sim 2) in at least one electrode and

relates to an electrochemical secondary battery made by using the electrode as at least one electrode.

If a specific example is given, the present invention relates to an electrode for secondary battery consisting of a polymer or a copolymer obtained by polymerizing or copolymerizing diphenylamine, triphenylamine and/or their derivatives and a secondary battery using the same.

An expectation for developing pollution-free electric automobiles has risen with emphasizing the pollution problem and energy problem. Development of a novel battery with light weight and high energy density is prospering therewith, thus attempts to apply new materials to electrodes have been made.

As a result, novel secondary batteries with polymeric compounds as electrodes have been developing more recently.

The present invention relates to these novel secondary batteries and electrodes using the same.

[Prior Art]

A battery with polymeric compounds as electrodes was realized for the first time by finding a doping method. If some kind of substance is doped by a doping operation into a high polymer which is originally an insulator, its

electroconductivity is markedly improved, and high polymers exhibiting electroconductivity in a semiconductor region or a good conductor region have been found one after another more recently. As their examples, polyacetylene, polyphenylene, polythiophene and polypyrrole, etc. are given. The following two methods have been generally adopted as methods for the doping operation.

- 1. Chemical doping method wherein substances exhibiting Lewis acidity (e.g., I_2 , PF_5 , SO_3 , $FeCl_3$, etc.) and alkali metals (Li, Na, K, etc.) are used in a method of contacting or mixing a dopant with a high polymer in a gas, liquid or solid phase.
- 2. Electrochemical doping method wherein a high polymer is brought into contact with an electrolyte in a liquid or a solid phase, a positive or a negative voltage is applied to the high polymer to dope a cation or an anion generated by ionic dissociation of the electrolyte.

In the above two methods, the electrochemical doping and dedoping of method 2 can be reversibly repeated, and this corresponds to charging and discharging of a secondary battery.

As described above, a new type of secondary batteries applied with a phenomenon of reversible electrochemical doping and dedoping have been invented one after another more recently.

For example, secondary batteries using an electrode based on polyacetylene (Japan Kokai 56-136469, Japan Kokai 57-121168,

/3

etc.), secondary batteries using an electrode based on poly-p-phenylene (Japan Kokai 58-112271, etc.) and secondary batteries using an electrode based on polythiophene (Japan Kokai 57-197759, etc.) are given.

[Problem to Be Solved by the Invention]

The inventors aimed at an organic polymer battery which can have a light weight and a high energy density, no pollution risk of using heavy metals such as cadmium, mercury, lead, etc., disused electrodes can be easily incinerated and give a future secondary battery using the electrodes, and they continued earnest studies that should develop a novel polymer battery.

Polyacetylene, polyphenylene, polythiophene, polythiazyl, etc. having a π -electron conjugated structure in main chain have been investigated as materials for prior well-known polymer batteries, but these substances are not melted even if they are heated, easily subjected to oxidative aging under heating and difficultly molded by common molding methods like thermoplastic resins in many cases. Almost no solvents dissolving these substances have been found yet. Accordingly, the productivity of

materials using these substances, which is taken as one of advantages of polymeric materials, is very low.

The first purpose of present invention is to provide an electrode made of a high polymer overcoming such disadvantage and a secondary battery using the same. The second purpose of present invention is to provide an electrode free from pollution problem of heavy metals and capable of easily incinerating disused electrodes and a secondary battery using the same. The third purpose of present invention is to provide a high-performance electrode which is handled more easily than the prior well-known polymer batteries and a secondary battery using the same.

(Means for Solving the Problems)

Namely, the substance of present invention consists in an electrode for an electrochemical secondary battery which is characterized by using a polymer of amines expressed by a general formula (I)

[here, X and Y are selected independently from a set composed of chlorine, bromine, iodine, methyl and ethyl groups, ℓ and m are

arbitrary integers selected independently within a range of 0 $^{\circ}$ 2, and then R is a hydrogen atom, an alkyl, an alkenyl and a $^{\circ}$ C₆H₆-(Z)_n group (Z is selected from a set composed of chlorine, bromine, iodine, methyl and ethyl groups, and then n is an arbitrary integer within a range of 0 $^{\circ}$ 2) in at least one electrode, and an electrochemical secondary battery using the electrode as at least one electrode.

As is evident from the above substance, high polymers used for electrode material in the present invention are polymers of amines expressed by the general formula (I), and preferably polymers of amines wherein ℓ and m are 0 and, in case of R = $-C_\ell H_\ell - (Z)_n$, n is also 0. Here, the polymers of amines not only include homopolymers of amines but also include copolymers of two or more amines expressed by the general formula (I). These polymer themselves are already well-known, for example, compounds expressed by the general formula (I) can be obtained by polymerization of amines according to Friedel-Crafts reaction with a Lewis acid catalyst such as ferric chloride, etc. or electrolytic polymerization of amines. The generated high molecules have a structure of repeated recombination of radicals generated by elimination of at least two hydrogen atoms from the compound of general formula (I), and then it has been made sure

that this elimination of hydrogen atoms is the elimination of almost all hydrogen atoms of phenyl nuclei.

According to Journal of Polymer Science, Part A-1, 10, 553 (1972), for example, structures of polymers obtained by polymerizing diphenylamine and triphenylamine contain the following structures, respectively. As is evident from these structural formulas, polymers used as construction material of electrode in the present invention hold no any conjugated electrons that can move for a long distance recognized in common in prior electrode materials such as polyacetylene, etc.

/4

The above formulas (1) \sim (4') do not mean that which one formula repeatedly appears in one polymer, they should be understood to show that the structures of (1) \sim (4) can appear

mixedly in case of using diphenylamine, the structures of (1) \sim (4') can appear mixedly in case of using triphenylamine, and the structures of (1) \sim (4') can appear mixedly in case of using the both. Although all the phenyl groups bound to N of triphenylamine are changed to phenylene groups to become a polymarization chain in the formulas (1) \sim (4'), in an ideal case, a part or most of three objective phenyl groups bound to N remain as phenyl groups intact in common polymerization conditions.

The above high polymers used in the present invention have thermal plasticity, are stable to thermal and air oxidation and are easily worked and molded in the shape of block, sheet, film, powder or an arbitrary shape without thermolysis and are dissolved in organic solvents such as dimethylformamide (DMF), dioxane, dimethyl sulfoxide, etc., therefore the polymers can also be worked into thin films from polymer solutions. Even if the polymers are polymers of triphenylamines, when they are polymerized under mild conditions or polymers having not so high degree of polymerization, they exhibit thermoplasticity and are soluble in solvents.

An ultrathin or thin electrode having low electric resistance and large surface area is obtained by adhering a metal to this ultrathin film by vapor deposition or by

impregnating the above polymer solution into a conductive fiber material such as carbon fiber fabric or paper, which enables to prepare a battery having a small interelectrode distance and a low internal resistance thereby.

The battery based on the present invention applies a principle of the latter electrochemical doping method in the above-mentioned two doping methods. Of course, the high-molecular polymers can also be doped by a chemical doping method or an electrochemical doping method with the purpose of improving the electroconductivity of high polymers used in the present invention.

To facilitate understanding of working mechanisms of the invented battery and electrodes, a case of polyacetylene battery working due to an electrochemically similar mechanism will be exemplified.

/5

When polyacetylene is used in both anode and cathode, a reactions at the anode are a charging reaction based on incorporation of an anion generated by dissociation of an electrolyte substance (salt) into polyacetylene and a discharging reaction based on emission of the anion (dedoping); and reactions at the positive electrode are a charging reaction

based on incorporation of a cation and a discharging reaction based on emission of the cation.

When polyacetylene is shown by (CH) $_{\rm n}$ and lithium perchlorate (LiClO $_{\rm d}$) is used as an electrolyte,

Anode reaction

$$(CH)_n + nxClO_4 \stackrel{Charge}{\leftrightarrows} [(CH)_{1-x}(CH^+)_x(C\ellO_4^-)_x]_n + nxe$$

Cathode reaction

$$(CH)_n + nxe + nxLi^+ = (CH)_{1-x}(CH^-)_x(Li^+)_n$$

$$\underset{Discharge}{\leftarrow} (CH)_{1-x}(CH^-)_x(Li^+)_n$$

Thus, the high polymers obtained by electrochemical oxidation or reduction function as anode or cathode of a secondary battery, therefore a secondary battery can be certainly constituted by combining with a cathode or an anode other than polyacetylene electrode or using polyacetylene in the both electrodes.

On the other hand, when polyacetylene is used as anode and lithium is used as cathode, reaction formulas are shown by the following formulas, respectively.

Anode reaction

(CH)_n +
$$nxClO_4^-$$
 = [(CH)_{1-x}(CH⁺)_x(C(O₄⁻)_x]_n + nxe

$$\lim_{n\to\infty} \frac{1}{n} \int_{\mathbb{R}^n} \frac{1}{n}$$

Cathode reaction

Charge

nxLi+ nxe ≒ nxLi Discharge

Although the mechanism for the amine polymers used in the present invention and working as electrodes has not been elucidated in detail yet and the present invention is not restricted anyway by the following description, the inventors has considered that the amine polymers work as electrodes by the following mechanism for the present. Namely, the following reaction is considered to take place in the charge-discharge process. If polydiphenylamine is taken as an example, the reaction is

(reaction formula, p5, lower left)

Charge -2e

+2e

Discharge

It is considered that doping occurs by an interaction of an $\mathrm{N}^{\scriptscriptstyle{+}}$ cation generated by the above formula and a perchloric acid anion (ClO4-) during charging, and the reverse reaction occurs during discharging.

When a substance same as anode is used as a cathode, lithium is presumed to intercalate between molecules of polymer, especially between a benzene ring and a benzene ring during charging in a reaction at the cathode. Of course, when a metallic material is used as cathode, it works due to deposition of metallic lithium on the cathode. When an electrolyte other than lithium perchlorate is used, it is similarly considered.

Polymeric compounds used in the present invention can also be used in either anode or cathode. When the invented electrode is used in either electrode, it had better be used as anode, in this case, the charge-discharge repeatability, charge-discharge coulomb efficiency, retentivity in the charged/discharged state and flatness during discharge are particularly excellent.

It is preferable that an auxiliary collector such as metal sheet, metal gauze, graphite, carbon fiber or the like is lined with the polymeric compounds based on the present invention or coexist therewith to reduce the internal resistance in assembly of battery.

Various electrolytes, such as dopants during electrochemical doping can be used in the invented battery, e.g., lithium perchlorate, LiBF $_4$, tetraalkylammonium perchlorate,

/6

 LiPF_{ϵ} , etc. are used as nonaqueous solvents dissolving these electrolytes, propylene carbonate, dichloromethane, tetrahydrofuran, etc. can be given. When the both electrodes used are stable to water, water can also be used as medium, in

this case, a wide range of electrolytes such as potassium iodide, etc. can be adopted as dopants. When a metal material is used as cathode, lithium is commonly used, but the metal is not limited to lithium, and other metals such as zinc, aluminum, etc. and, under certain circumstances, carbon can also be used depending upon electrolytes used.

When metallic lithium is used as cathode in the invented battery, the battery must be kept under argon atmosphere. Atmospheres other than argon can also be used depending upon materials of cathode and kind of electrolytes used, but the use of argon atmosphere is generally reliable.

The invented battery can be used at a high level of 150 ~ 200 watt≅hr in energy density (output) per 1 kg of electrode material. This energy density is somewhat inferior to the energy density of 200 ~ 300 watt≅hr/kg of the famous polyacetylene battery, but it is a fairly high energy density. Then, the electrode materials of present invention are thermoplastic and soluble in solvents, if it is considered that they can be easily molded into any desired shapes, such as moldings of complicated structures or film, etc., their use value is extremely high.

(Actual Examples)

The present invention will be described more specifically by showing actual examples below, but they are simply exemplified and do not limit the present invention.

Actual Example 1

A battery having a sandwich structure as shown in Fig. 1 and Fig. 2 was assembled by using a fine powder of a high polymer in he present invention, a fiber based on carbon (tradename Carboron, made by Nippon Carbon Co.) as a collector and a glass fiber filter paper as a diaphragm.

Fig. 1 is a schematic illustrative diagram shows the constitution of a battery used in this actual example, and Fig. 2 is a development thereof.

1 and 9 are collecting terminals, 2 and 8 are collectors (both are 12×17 mm rectangles of 0.31 mm in thickness), 3 and 6 are glass fiber filter papers and are opened with a rectangular window at the center, respectively and 100 mg of polydiphenylamine (4 and 7) is packed therein, and 5 represents a glass fiber filter paper diaphragm, respectively. 10 is a teflon sheet, and then 11 is a 32 mm-diameter polyethylene container. The purpose of providing the teflon sheet 10 is to disperse a pressing force from the top to the whole with screws

to improve and uniformize the contact of each layer of battery and not allow the screws to get into touch with the battery.

After the battery was assembled, 3 mL of a propylene carbonate solution of lithium perchlorate (1 mol/L) was added to immerse the teflon sheet 10 in a state that the battery is pressed from the top, then a charge-discharge test was carried out. Moreover, all of the assembly of battery and the charge-discharge test, etc. were carried out under argon atmosphere.

The battery was charged by allowing a constant current of 1.0 mA to continuously flow for 60 min to both ends of the collecting terminals and then discharged at a constant current of 0.5 mA, when the terminal voltage became 0.1 V, the discharge was stopped. A result shown below was obtained by repeating this cycle 10 times. Moreover, if the 10th cycle is described as an example, the terminal voltage indicated 3.1 V immediately after the start of charge, when it slowly rose and became 3.8 V after 60 min, the charge was stopped and the discharge was performed. The terminal voltage was 3.3 V immediately after the start of discharge, when it slowly dropped and became 1.0 V after 87 min, the discharge was stopped.

	Char		Disch	narge	Charge-	
				Final	Discharge	
Cycle	Initial	Final	Initial	voltage	Coulomb	
	voltage	voltage	voltage	of flat part	Efficiency	
	(∀)	(V)	(V)	(V)		
					(%)	
1	3.0	3.3	3.0	2.3	28	
2	2.8	3.4	3.2	2.5	58	
3	2.8	3.4	3.2	2.5	66	
4	2.8	3.4	3.2	2.5	68	
6	2.8	3.5	3.2	2.2	67	
8	2.9	3.7	3.3	2.1	71	
10	3.1	3.8	3.3	2.1	73	

Polydiphenylamine used in the present invention was synthesized according to *Journal of Polymer Science*, Part A-1, 10, 553 (1972) and was obtained by polymerizing diphenylamine with ferric chloride as catalyst, and it was a greenish gray solid.

Actual Example 2

A battery similar to Actual Example 1 was assembled except that 100 mg of polydiphenylamine powder was used as anode and a lithium foil (a 10 \times 15 mm rectangle of 0.2 mm in thickness) was used in cathode, and then a charge-discharge test was carried oit. The following result was obtained by repeating a cycle 26 times in which the battery was charged for 60 min at a constant current of 1 mA and discharged at a constant current of 0.5 mA until the terminal voltage became 1.0 V. If the 25th cycle is described as an example, the terminal voltage slowly rose from

3.1 V immediately after the start of charge, when it reached 3.4 V after 60 min, the battery came into the discharge process; the terminal voltage slowly dropped and became 2.8 V after 106 min from the start of discharge, when it suddenly dropped and reached 1.0 V in 117 min after the start of discharge, the discharge was stopped. In the 26th cycle, the battery was charged for 60 min at a constant current of 1.0 mA, subsequently allowed to stand for 72 hr and then discharged was at a constant current of 0.5 mA.

	Cha	rge	rge Disch		Charge-
				Final	Discharge
Cycle	Initial	Final	Initial	voltage	Coulomb
	voltage	voltage	voltage	of flat part	Efficiency
	(V)	(V)	(V)	(V)	
					(%)
1	3.1	3.2	3.3	3.1	66
2	2.9	3.2	3.3	3.0	73
5	2.9	3.3	3.3	2.9	82
10	3.2	3.5	3.2	2.8	91
1.5	3.2	3.5	3.3	2.8	93
20	3.1	3.4	3.3	2.8	93
25	3.1	3.4	3.4	2.8	98
26	3.0	3.4	3.1	2.8	58

Actual Example 3

A battery similar to Actual Example 1 was assembled except that 50 mg of polytriphenylamine was used in place of 100 mg of polydiphenylamine in Actual Example 1 and then a charge-discharge test was carried out. The following result was obtained by repeating a charge-discharge cycle 10 times. If the 10th cycle is described as an example, the terminal voltage indicated 3.4 V immediately after the start of charge, but it slowly rose and became 4.0 V after 60 min, it was 3.5 V just after coming into the discharge process and then became 2.5 V after 67 min since the start of discharge, subsequently it suddenly dropped and became 1.0 V after 73 min since the start of discharge, and the discharge was stopped.

	Charge		Disc	Charge-	
Cycle	Initial voltage (V)	Final voltage (V)	Initial voltage (V)	Final voltage of flat part (V)	Discharge Coulomb Efficiency (%)
1	3.1	3.5	3.2	2.9	38
2	3.0	3.7	3.4	3.0	54
4	3.2	3.8	3.4	2.9	55
6	3.3	3.9	3.5	2.8	59
8	3.3	4.0	3.5	2.7	63
1.0	3.4	4.0	3.5	2.5	61

Polytriphenylamine used in the present invention was synthesized according to *Journal of Polymer Science*, Part A-1, 7, 3229 (1969) and was similarly obtained as polydiphenylamine

/8

by polymerizing triphenylamine with ferric chloride as catalyst, and it was a greenish gray solid.

Actual Example 4

A battery similar to Actual Example 2 was assembled except that 50 mg of polytriphenylamine powder was used in place of 100 mg of polydiphenylamine powder in Actual Example 2, and then a charge-discharge test was carried out. When the battery was charged for 60 min at a constant current of 1.0 mA and then discharged at a constant current of 0.5 mA, when the terminal voltage became 1.0 V, the discharge was stopped. The following result was obtained by repeating such a cycle 28 times. If the 28th cycle is described as an example, the terminal voltage indicated 4.3 V immediately after the start of charge, but it slowly rose, when it became 4.6 V after 60 min, the discharge was stopped and the discharge was started. The terminal voltage indicated 3.5 V immediately after the start of discharge, but it slowly rose and became 3.0 V after 58 min, then it suddenly dropped to 1.7 V. Subsequently, it continued to slowly drop,

when it reached 1.0 V after 117 min since the start of discharge, the discharge was stopped.

	Charge		Disc	Charge-	
Cycle	Initial voltage (V)	Final voltage (V)	Initial voltage (V)	Final voltage of flat part (V)	Discharge Coulomb Efficiency
1	4.3	4.3	3.3	-	38
2	4.2	4.3	3.4	3.0	53
5	4.2	4.4	3.5	3.2	73
10	4.2	4.4	3.5	3.2	89
15	4.3	4.5	3.5	3.1	83
20	4.3	4.6	3.5	3.0	90
25	4.3	4.6	3.4	3.0	92
28	4.3	4.6	3.5	3.0	98

Actual Example 5

4 mL of a dimethylformamide solution containing 0.105 g of polydiphenylamine was impregnated into a fiber paper based on carbon (it is a 20 \times 165 mm rectangle, and 5 \times 5 mm terminals were attached to both ends), and then used for anode by evaporating dimethylformamide and completely removing it. An aluminum foil of the same size and same type as the anode was used for cathode. Two pieces of glass fiber filter paper (20 \times 165 mm rectangles) were used as diaphragm so that the anode and the cathode were not in direct touch with each other. The anode, glass fiber filter paper, cathode and glass fiber filter paper were stacked in this order. This state was typically shown in

Fig. 3. Although the anode 12, glass fiber filter paper diaphragm 13, cathode 14 and glass fiber filter paper diaphragm 15 are actually stacked, they are shown by slightly shifting their positions for the convenience of drawing in Fig. 3. Next, the whole was rounded into a circular cylinder and then charged into a cylindrical glass container of 18 mm in inside diameter and 25 mm in height to assemble a battery. Next, 5.5 mL of a propylene carbonate solution (1 mol/L) of lithium perchlorate was added and then a charge-discharge test was carried out.

The battery was continuously charged by allowing a constant current of 2 \sim 20 mA to flow to the anode and cathode for 10 \sim 60 min. A result as the following table was obtained by repeating such a cycle 100 times. A self-discharge test was carried out in the 91th cycle. The coulomb efficiency after putting on shelf for 20 hr (1,200 min) was 84.5%, and the self-discharge was little. A short-circuit current obtained when the

(left half)

		Ch	arge		Pause
Cycle	Current	Time	Initial	Final voltage in	Pause
			Voltage	flat part	time
	(mA)	(min)	(V)	(V)	(min)
1	2.0	10.0	3.3	3.3	-
2	3.0	30.0	3.3	3.4	-
4	5.0	60.0	3.4	3.6	-
12	5.0	60.0	3.4	3.7	-
13	7.0	60.0	3.5	3.8	-
15	10.0	40.0	3.7	4.0	-
16	7.0	60.0	3.5	3.8	-
34	7.0	60.0	3.6	4.2	-
35	7.0	40.0	3.6	3.9	20.0
4.9	7.0	40.0	3.6	4.0	-
55	20.0	15.0	4.2	6.0	5.0
60	5.0	20.0	3.5	3.7	10.0
70	5.0	20.0	3.7	3.8	10.0
80	5.0	20.0	3.8	4.2	10.0
91	5.0	20.0	3.7	3.8	1,200.0
100	5.0	30.0	3.6	3.8	10.0

(right half)

			Discharge			Charge-
				Final		Discharge
Cycle	Current	Time	Initial	voltage In	Stop	Coulumb
			Voltage	flat part	voltage*	Efficiency
	(mA)	(min)	(V)	(V)	(V)	(%)
1	1.0	14.0	3.0	2.8	1.0	70.0
2	2.0	29.0	3.0	2.7	1.0	64.5
4	5.0	34.2	2.9	2.5	1.0	57.0
1.2	5.0	43.0	3.2	2.5	1.0	71.6
13	7.0	35.0	3.1	2.4	1.0	58.3
15	10.0	27.5	3.0	2.2	1.0	68.8
1.6	10.0	28.0	3.0	2.2	1.0	66.7
34	7.0	51.0	3.3	2.5	1.0	85.0
35	7.0	35.0	3.2	2.6	1.0	87.5
49	7.0	37.0	3.3	2.5	1.0	92.5
55	20.0	13.0	2.4	2.2	1.0	65.0
60	5.0	17.5	3.0	2.8	1.0	87.5
70	5.0	18.0	3.2	3.0	1.0	90.0
80	5.0	18.0	3.2	3.1	1.0	90.0
91	2.0	42.25	3.3	3.1	1.0	84.5
100	2.0	68.0	3.3	3.0	0.0	91.0

 $^{^\}star$ Discharge stop voltage: A stop voltage 1.0 V indicates that the voltage during discharge was reduced to 1.0 V followed by coming into the next charging process.

(Effects of the Invention)

The high polymers which are electrode material for the invented electrode and battery are different from prior well-known materials for polymer batteries and they have thermoplasticity and soluble in solvents, therefore they are easy to give a thin film excellent in moldability and can find wide range of applications, such as a battery having an instantaneous power while being a small volume as a structure of paper condenser, a battery which essentially does not require an

installation space of battery while being a large capacity by pasting it on the surface of structure, a battery having a complicated comb-like or various condenser-like structures in a small volume. Moreover, the invented battery and electrodes have no concern about heavy metal pollution and disused battery is easily incinerated if it is disused.

IV. Brief Description of the Drawings

Fig. 1 is a schematic illustrative diagram showing the constitution of battery used in this actual example, Fig. 2 is its development, and then Fig. 3 is an illustrative diagram typically showing the structure in a state of expanding an electrode used in Actual Example 5.

1, 9 collecting terminals 2, 8 J collectors 3, 6 J glass fiber filter papers electrode materials glass fiber filter paper diaphragm 10 teflon sheet 1.1 container 12 anode 13, 15 glass fiber filter paper diaphragm 14 cathode

/10





Fig. 2

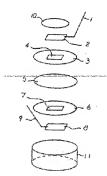


Fig. 3

